

# Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US05/009590

International filing date: 21 March 2005 (21.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US  
Number: 60/555,353  
Filing date: 22 March 2004 (22.03.2004)

Date of receipt at the International Bureau: 29 April 2005 (29.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1310664

# THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

*April 19, 2005*

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.**

**APPLICATION NUMBER: 60/555,353**

**FILING DATE: *March 22, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US05/09590***



Certified by

Under Secretary of Commerce  
for Intellectual Property  
and Director of the United States  
Patent and Trademark Office



20427 U.S. PTO

032204

PTO/SB/16 (01-04)

Approved for use through 07/31/2006. OMB 0651-0032  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

## PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. ET662093105US

22151 U.S. PTO  
60/555353

032204

INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
George Albert		Farthing, Jr.		Alliance, Oh	
Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
BROMINE ADDITION FOR THE IMPROVED REMOVAL OF MERCURY FROM FLUE GAS					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number:		000041669			
OR					
<input type="checkbox"/> Firm or Individual Name					
Address					
Address					
City		State		Zip	
Country		Telephone		Fax	
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages 7		<input type="checkbox"/> CD(s), Number _____			
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets 3		<input type="checkbox"/> Other (specify) _____			
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE Amount (\$)	
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees.				160.00	
<input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 50-1831					
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

[Page 1 of 2]

Respectfully submitted

SIGNATURE

TYPED or PRINTED NAME Michael J Seymour

TELEPHONE (330) 860-6605

Date March, 22, 2004

REGISTRATION NO. 54,436

(if appropriate)

Docket Number: Case 7103

## USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

**PROVISIONAL APPLICATION COVER SHEET**  
**Additional Page**

PTO/SB/16 (08-03)

Approved for use through 07/31/2006. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Docket Number Case 7103

INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle [if any] )	Family or Surname	Residence (City and either State or Foreign Country)
William	Downs	Alliance, Ohio

[Page 2 of 2]

Number 1 of 1

**WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

## **BROMINE ADDITION FOR THE IMPROVED REMOVAL OF MERCURY FROM FLUE GAS**

### **[001] BACKGROUND OF INVENTION**

[002] Emissions Standards, as articulated by the U.S. Environmental Protection Agency (EPA), require assessment of hazardous air pollutants from utility power plants. Coal-fired utility boilers are a known source of anthropogenic mercury emissions in the United States. The EPA recently articulated the need to regulate mercury emissions from coal- and oil-fired utility units.

Accordingly as elemental mercury and many of its compounds are volatile, conventional electric utility plant air pollution control methods fail to meet advancing EPA standard requiring new methods and processes to be developed.

[003] Mercury appears in coal combustion flue gases in both the solid and gas phases, particulate-bound mercury and vapor-phase mercury, respectively. Due to the high volatility of mercury and many of its compounds, most of the mercury found in flue gases is vapor-phase mercury. Vapor-phase mercury, can appear as elemental mercury (elemental, metallic mercury vapor) or as oxidized mercury (vapor-phase species of various compounds of mercury). Speciation, the form of mercury present, is a key factor in the development of mercury emissions control strategies.

[004] Particulate collectors in use at electric utility plants, most commonly electrostatic precipitators (ESP) or fabric filters (FF), sometimes called baghouses, provide high-efficiency removal of particulate-bound mercury. Fabric filters tend to exhibit better mercury removal than ESP's by providing more intimate contact between the flue gases and fly ash as the flue gases pass through the filter cake of fly ash on the filter bags. This intimate contact may promote the adsorption of vapor-phase mercury species onto the fly ash or unburned carbon particles in the

Date Filed: Filed March 22, 2004

Title: BROMINE ADDITION FOR THE IMPROVED REMOVAL OF MERCURY FROM FLUE GAS

filter cake. Both wet and spray dryer absorber (SDA) flue gas desulfurization (FGD) systems remove significant amounts of oxidized mercury. Oxidized mercury, typically appearing in the form of mercuric chloride, is soluble in water, making it amenable to removal in sulfur dioxide scrubbers. Elemental mercury, insoluble in water, passes through most scrubbers. Removal of elemental mercury, therefore, remains an important issue in the search for cost-effective mercury control techniques.

[005] Numerous studies have been, and continue to be, conducted to develop cost-effective approaches to the control of elemental mercury. Many of the studies have focused on the injection of a carbonaceous sorbent (e.g., powdered activated carbon, or PAC) into the flue gas stream to adsorb vapor-phase mercury. The sorbent, and its burden of adsorbed mercury, are subsequently removed from the flue gases in a downstream particulate collector. Adsorption is a technique that has often been successfully applied for the separation and removal of trace quantities of undesirable components. PAC injection is used, commercially, to remove mercury from municipal waste combustor exhaust gases. PAC injection removes both oxidized and elemental mercury species, although removal efficiencies are higher for the oxidized form. Although this approach appeared attractive in early work, the economics of high injection rates can be prohibitive when applied to coal-fired utility plants. More refined studies are now in progress to define more precisely what can and cannot be achieved with PAC. Still other studies seek to enhance PAC technology. One technique subjects the PAC to an impregnation process wherein elements such as iodine or sulfur are incorporated into the carbonaceous sorbent. Such processes can yield sorbents that more strongly bond with adsorbed mercury species, but also result in significantly higher sorbent cost.

[006] The speciation of vapor-phase mercury depends on coal type. Eastern U.S. bituminous coals tend to produce a higher percentage of oxidized mercury than do western subbituminous and lignite coals. Western coals have low chloride content compared to typical eastern bituminous coals. It has been recognized for several years that a loose empirical relationship holds between the chloride content of coal and the extent to which mercury appears in the oxidized form. Figure 1 illustrates the relationship between coal chlorine content and vapor-phase mercury speciation. An important reason for the significant uncertainty (scatter) in the data of Figure 1 is that mercury oxidation proceeds by both homogeneous and heterogeneous reaction mechanisms. Boiler convection pass and combustion air preheater temperature profiles, flue gas composition, fly ash characteristics and composition, and the presence of unburned carbon have all been shown to affect the conversion of elemental mercury to oxidized mercury species.

[007] Felsvang, et. al. (U.S. Patent 5,435,980), teaches that the mercury removal of a coal-fired system employing an SDA FGD system can be enhanced by the addition of a chlorine-containing agent to the coal, or to the combustion zone of the of the boiler furnace. Felsvang, et. al., further teaches that the chlorine content of the flue gases reaching the SDA can also be raised through the injection of hydrochloric acid (HCl) vapor into the flue gases upstream of the SDA. Finally, Felsvang, et. al., teaches that increasing the chlorine content of the flue gases by either means can improve the mercury removal performance of PAC when used in conjunction with an SDA FGD system.

#### [008] SUMMARY OF THE INVENTION

[009] It is an object of this invention to invention to yield significant technical and commercial advantages over the prior art. The inventors have determined through experimental testing that

the use of bromine-containing compounds, added to the coal, or to the boiler combustion furnace, are significantly more effective than chlorine-containing compounds in enhancing the oxidation of mercury, thereby enhancing the overall removal of mercury in downstream pollution control devices. Second, the technique is applicable to utility power plants equipped with wet FGD systems, as well as those plants equipped with SDA FGD systems. Wet FGD is the sulfur dioxide removal system of choice for most coal-fired utilities around the world. Approximately 25% of the coal-fired electric power plants in the U.S. are equipped with wet FGD systems.

#### **[0010] BRIEF DESCRIPTION OF THE DRAWINGS**

**[0011]** Fig. 1 is Relationship between coal mercury content and mercury speciation for U.S. coals.

**[0012]** Fig. 2 is a view of Bromine Addition for the Improved Removal of Mercury from Flue Gases

**[0013]** Fig. 3 is a Mercury Removal with Calcium Bromide Addition chart

**[0014]** Fig. 4 is a Coal-Fired Utility Plant Equipped with a Particulate Collector

**[0015]** Fig. 5 is a Coal-Fired Utility Plant Equipped with an SDA FGD and Particulate Collector

**[0016]** Fig. 6 is a Coal-Fired Utility Plant Equipped with a Wet FGD and Particulate Collector

#### **[0017] DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**



[0018] The preferred embodiment of the current invention is illustrated in Figure 2. A bromine-containing reagent is added to the boiler combustion furnace, either directly or by premixing with the incoming coal. Bromine species released during the combustion process enhance the oxidation of mercury as the combustion gases pass through the furnace and, in particular, through the cooler sections of the boiler convection pass and combustion air preheater. The increased fraction of mercury appearing in the oxidized form enhances mercury removal in downstream pollution control systems such as wet and SDA FGD systems, and PAC injection systems. As is described herein, experimental results indicate that bromine addition also results in an increased fraction of particulate-bound mercury. This enhances removal of mercury across particulate collectors such as fabric filters and electrostatic precipitators.

[0019] The removal of elemental mercury from coal combustion gases generated by electric utility plants through the application of a conventional PAC injection process is very expensive. The current invention promises to significantly reduce the cost of mercury removal at coal-fired electric plants in two ways. First, increasing the fraction of mercury appearing in the oxidized and particulate-bound forms enhances the removal of mercury in conventional pollution control systems such as particulate collectors and wet and SDA FGD systems. This reduces, or may eliminate entirely, the need for PAC injection to remove elemental mercury. Second, the increased fraction of oxidized mercury also enhances the removal of mercury across a PAC injection process, due to the higher reactivity of oxidized mercury with PAC.

[0020] The invention was tested in a 5 million Btu/hr Small Boiler Simulator (SBS) Facility. The SBS was fired at approximately 4.3 million Btu/hr with a western U.S. subbituminous coal. During the tests flue gases exiting the SBS boiler first passed through a spray dryer absorber

(SDA) for removal of sulfur dioxide, and then through a fabric filter for removal of fly ash and spent sorbent from the SDA FGD system.

[0021] An aqueous solution of calcium bromide ( $\text{CaBr}_2$ ) was injected into the combustion chamber through the coal burner. Figure 3 illustrates the removal of mercury across the SDA/FF system. It can be seen that upon injection of the calcium bromide, the vapor-phase mercury exiting the system dropped from its initial value of approximately 6 ug/dscm to about 2 ug/dscm. It can also be seen that the vapor-phase mercury at the system inlet also drops upon addition of the calcium bromide. This is due to the fact that the calcium bromide also enhances the formation of particulate-bound mercury (Particulate-bound mercury does not appear on the chart, since the on-line mercury analyzer being used only detects vapor-phase mercury species.). These results identify that the current invention can offer a cost-effective method of removing elemental mercury from coal combustion flue gases.

[0022] In the preferred embodiment, an aqueous solution of calcium bromide is sprayed onto the crushed coal before the coal is pulverized for combustion. The aqueous solution is easily handled and metered onto the coal, the coal pulverizers intimately mix the bromide reagent with the coal, and the pulverized coal conveying system to the several coal burners ensures an even distribution of the reagent across the boiler furnace. There are many alternative ways to implement the invention as would be gleamed by one of skill in the art.

[0023] In another embodiment the boiler fuel may be fired with, thus include, bituminous, subbituminous, and lignite coals and blends, thereof.

[0024] In yet another embodiment, the bromine-containing reagent could comprise, but is not limited to, alkali metal and alkaline earth metal bromides hydrogen bromide gas ( $\text{HBr}$ ) or bromine ( $\text{Br}_2$ ), or acids.

[0025] In yet another embodiment the bromine-containing reagent may be fed to the boiler combustion zone in gaseous, liquid, or solid form.

[0026] In yet another embodiment, the electric utility plant configurations may include plants equipped with an SDA FGD and particulate collector (Figure 4), a particulate collector (Figure 5), and a wet FGD and particulate collector (Figure 6).

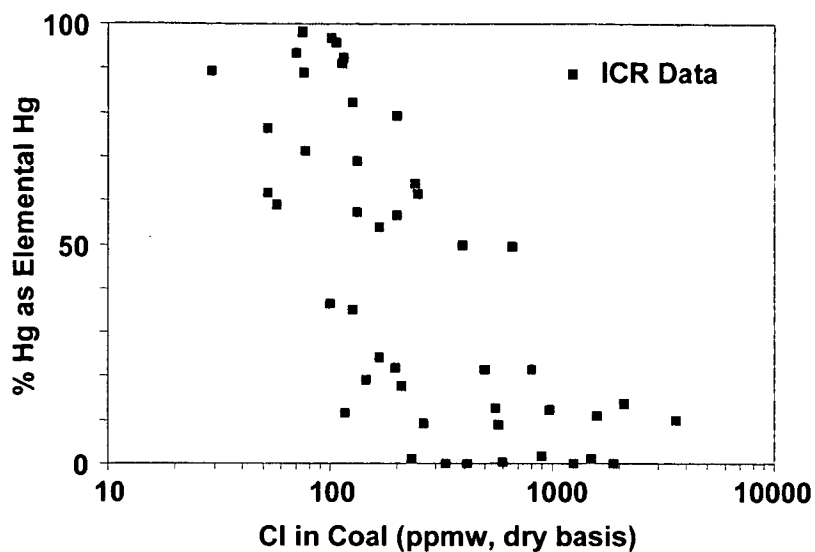
[0027] In yet another embodiment, the invention may be utilized in a plant equipped with an SCR system for the control of nitrogen oxides, as SCR catalysts have been shown to promote the oxidation of elemental mercury if the correct species (in this case bromine species) are present in the flue gases.

[0028] In yet another embodiment mercury removal may be further enhanced by utilizing a sorbent injection system in conjunction with the present invention. Such carbonaceous sorbents include, but are not limited to, powdered activated carbon (PAC), carbons and chars produced from coal and other organic materials, and unburned carbon produced by the combustion process itself.

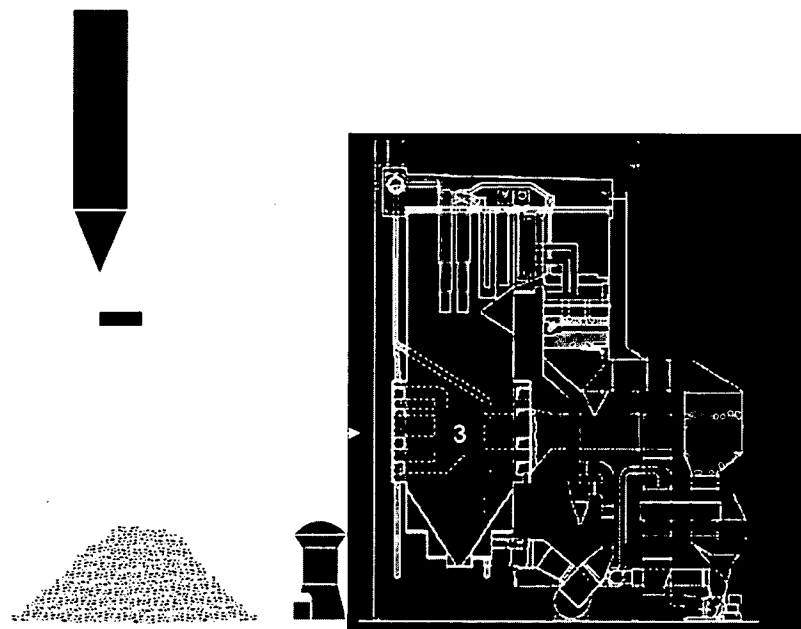
[0029] There are other alternative embodiments as would be obvious to one of skill in the art based on the teaching of the present invention, and are intended to be included within the scope of the claims of this invention.

I claim:

1. A method of reducing the mercury concentration of a flue gas comprising;  
adding a bromine containing agent to the combustion chamber.
2. A method of reducing the mercury concentration of a flue gas comprising the method as recited herein.



**Fig. 1 Relationship Between Coal Chlorine Content and Mercury Speciation for U.S. Steam Coals**  
Source: Senior, C.L., *Behavior of Mercury in Air Pollution Control Devices on Coal-Fired Utility Boilers*, 2001



**Fig. 2 Bromine Addition for the Improved Removal of Mercury from Flue Gases**

BEST AVAILABLE COPY

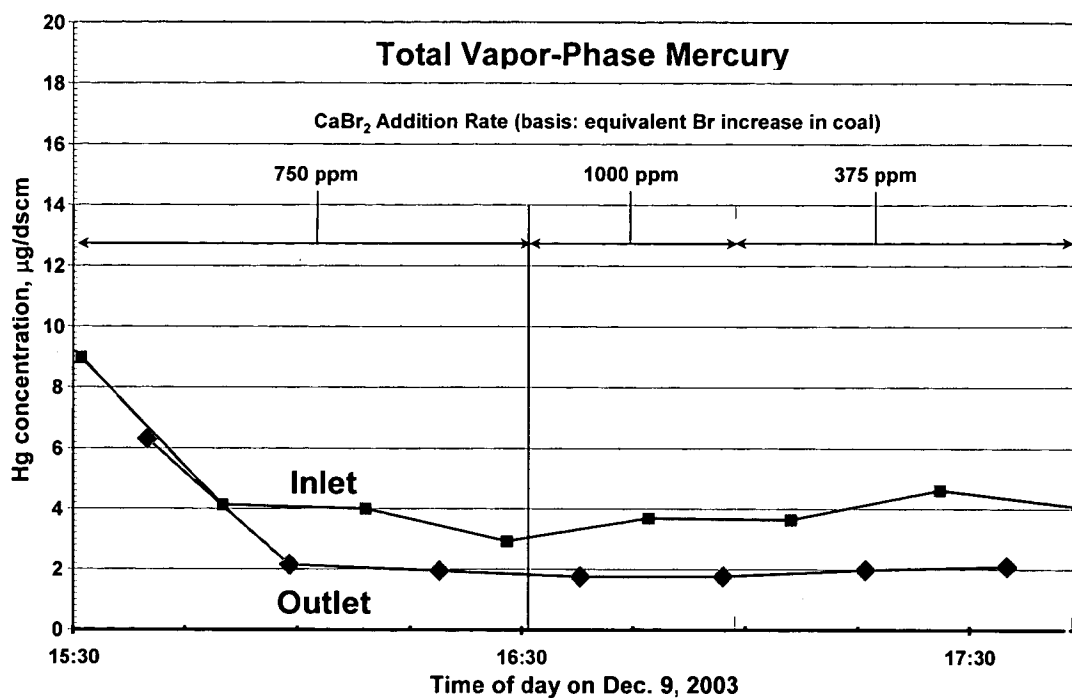


Figure 3 Mercury Removal with Calcium Bromide Addition

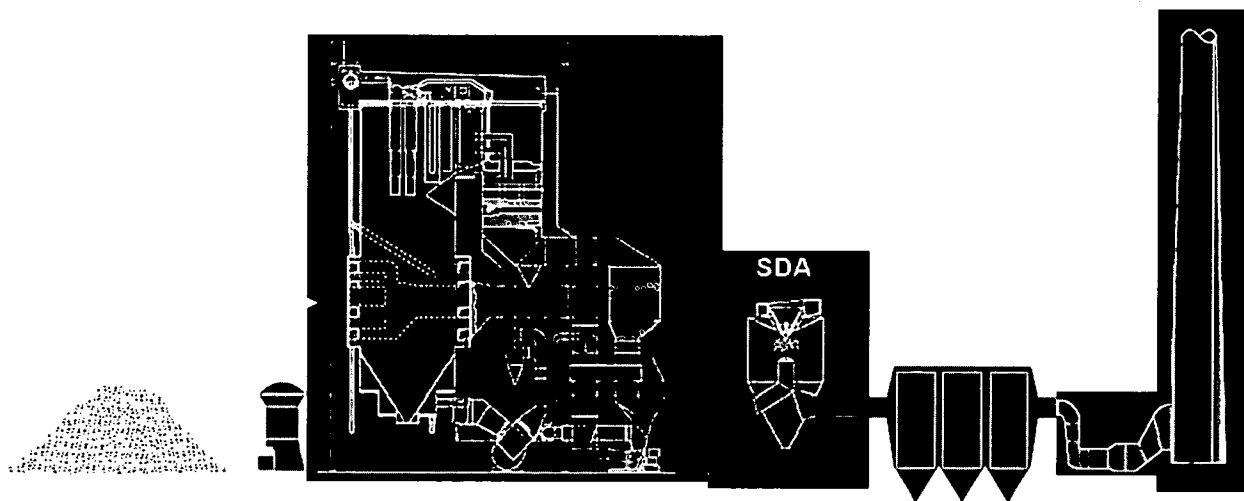


Fig 4 Coal-Fired Utility Plant Equipped with an SDA FGD and Particulate Collector

BEST AVAILABLE COPY

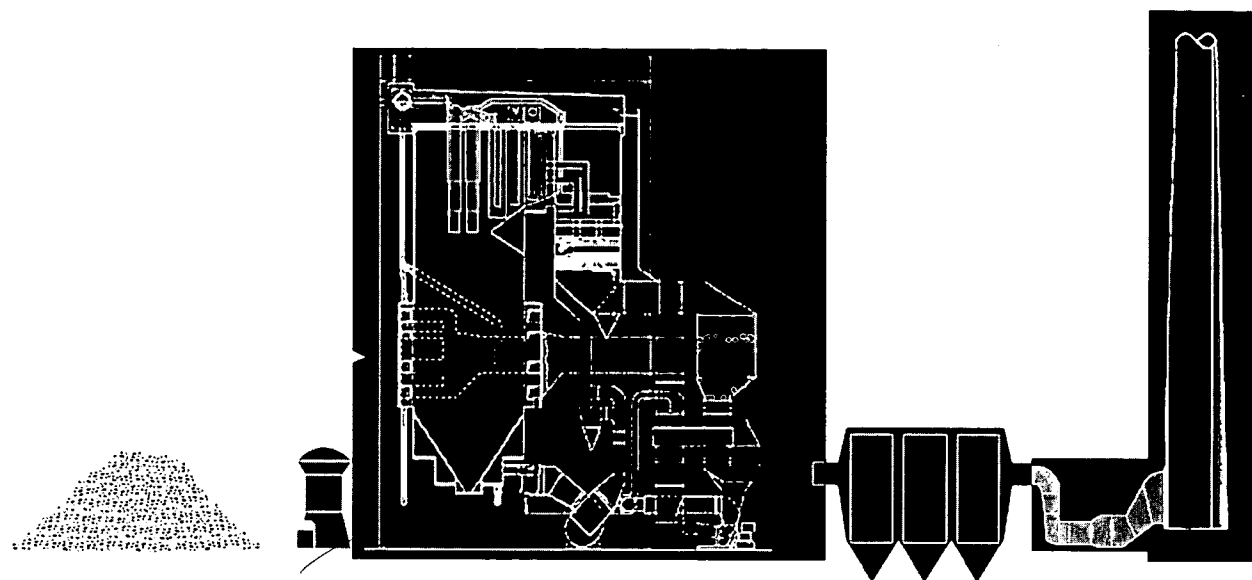


Fig 5 Coal-Fired Utility Plant Equipped with a Particulate Collector, Only

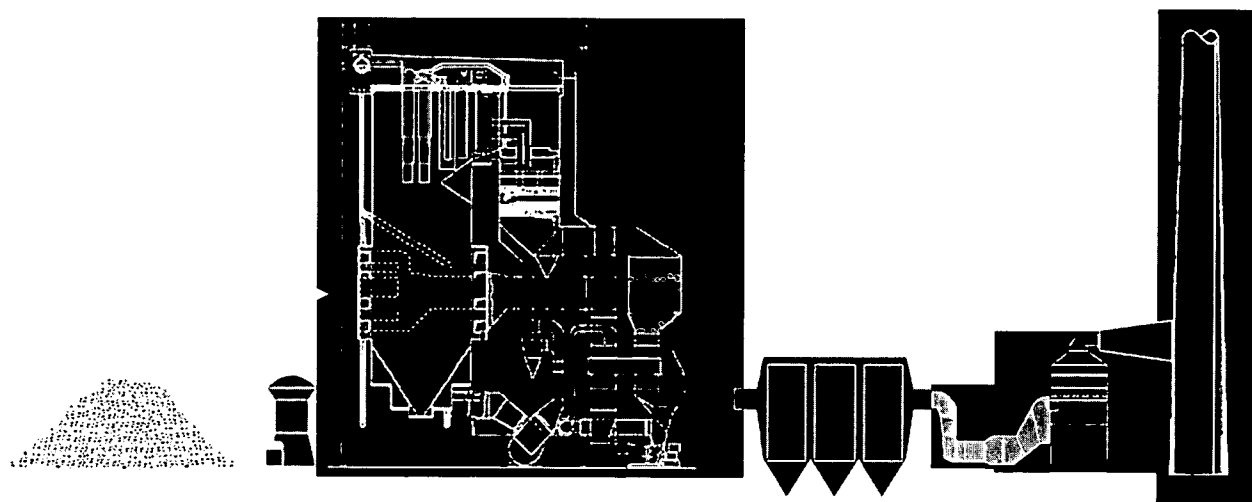


Fig 6 Coal-Fired Utility Plant Equipped with a Wet FGD and Particulate Collector

BEST AVAILABLE COPY